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(54) Selective plating method

(57) The invention relates to a process for providing objects with a metal plating. More specifically it relates to electrolytically plating of objects, which objects comprise areas that should be plated and areas that should not be plated. It has been found that the ratio between the thickness of the plating layer on the areas that should not be plated, and the areas that should be plated can be lowered by first plating both areas and then removing parts of the plated layers by stripping.

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Description

[0001] The invention relates to a process for providing objects with a metal plating. More specifically it relates to electrolytically plating of objects, which objects have shapes that may result in a non-uniform current density distribution during electrolytic processes. Such objects can for instance be objects with an inner and an outer surface, for example cylinders, sockets, cup-shaped objects and flat objects comprising holes, but also objects with an outer surface only, such as connector pins, or even flat surfaces such as metal strips where, dictated by geometry, metal(gold) may be plated on unwanted area.

[0002] When plating conductive objects electrolytically, it is often desirable to control the selectivity of the plating in order to obtain objects with plating layers of varying thickness for various areas.

[0003] In plating processes the object to be plated is electrically contacted to the cathode, and is immersed in a solution comprising cations of the plating metal. The counter electrode is also immersed in the solution. When a current is passed from the anode to the cathode, the ions from the solution will be reduced on the surface of the cathodic object, and the plating is thus formed.

[0004] When the objects to be plated are non-uniform in shape, this will give differences in current density over the surface area of the objects. That is, the current density, expressed in amperes per unit area, has a gradient along the surface of the object. This will result in different plating rates across the surface of the object and as a result differences in plating thickness will occur. When mention is made of a non-uniform object herein, it shall be understood that an object having a shape that gives rise to a substantially non-uniform current density distribution in an electrolytic process is meant. Such a distribution is to be regarded substantially non-uniform when in an electrolytic plating process it would give rise to substantial differences in plating thickness. The distribution factor DF is the ratio of the thickness of the metal layer plated on unwanted areas to the thickness of the metal layer plated on wanted area, and generally is substantially larger than 1, more specifically larger than 2.

[0005] In electrolytic plating processes of non-uniform objects the plating rate will normally be higher on the areas of the objects where the current density is higher. This can be a problem when it is desired that the thickness of the plating at areas of a low current density is higher than that of areas with a high current density.

[0006] In the art several methods for selective electrolytic plating or plating of non-uniform objects are known. For example, US-A-5,476,581 relates to a method for producing a weapon barrel having a wear resistant inner coating. The inner surface of a prefabricated weapon barrel is subjected to an electrolytic polishing process, followed by an electrolytic plating process. The cathode is placed inside the barrel in order to obtain the required selectivity, i.c. a coating on the inside of the barrel.

[0007] US-A-5,372,700 teaches a method for selective electrolytic deposition of a metal such as gold onto the inside surface of a bush type hollow body. The selectivity is obtained by injecting the electrolytic solution inside the hollow body and passing a current between the bush and an electrode in electrical contact with the solution.

[0008] US-A-5,516,415 and US-A-5,527,445 relate to processes for electroforming a structural layer of metal bonded to an internal wall of a metal tube. Deposition on the inside of the tube is obtained by inserting a probe and moving it to span the desired sections.

[0009] All these methods use electrodes that are placed near the surface to be plated, while the surface which is not to be plated is shielded from the plating process. Such methods are only useful in plating relatively large and uniformly shaped and uncomplicatedly formed objects.

[0010] It has now been found that metal distribution on non-uniform objects can be improved by first forming a plating on the surfaces or selected parts of the surfaces of the objects in an electrolytic plating process yielding a certain DF value, which preferably is as low as possible, followed by stripping of the initial plating in an electrolytic stripping process using a stripping solution under such conditions that the DF value is lowered. The stripping rate depends e.g. on the non-uniform current density distribution on each of said objects, and the chemistry of the stripping solutions.

[0011] Because of the stripping step, the initial plating will have to result in thicker plating layers than required in the final product.

[0012] More in detail, the present invention relates to a process for plating an object, having wanted and unwanted areas to be plated, comprising the steps of

a) forming in a plating bath of a plating on the surface or a selected part of the surface of said object, yielding a certain DF value;

b) partially restripping of the plating of step a) in an electrolytic stripping process using a stripping solution under such conditions that said DF value is lowered.

[0013] In a preferred embodiment, which is especially suitable for plating objects which have shapes resulting in a non-uniform current density distribution during electrolytic processes, which objects are exemplified in the first paragraph of this specification, the total surface of the non-uniform object is plated yielding a certain DF value, which

preferably is close to 1, and subsequently is stripped wherein the DF value is lowered through a difference in current distribution and efficiency during stripping. After the stripping step, the DF value preferably is much lower than 1, and more preferably lower than 0.5.

[0014] The DF value can also be improved or can be further lowered by e.g. controlled immersion stripping of for example connector pins when no deposit is required on the connector tip or by means of masking techniques where only unwanted areas of the originally plated spot are exposed to the stripping solution for example spot plating and subsequent spot stripping yielding a nett improved selectivity for metal deposition.

[0015] In a second preferred embodiment the object is fully or partly immersed in a plating bath and subsequently partly immersed in a stripping solution. This embodiment can suitably be carried out in a so-called reel to reel connector or lead frame line. The immersion of the plated object in the stripping bath is controlled in such a way that only a part of the surface plated is subjected to stripping.

[0016] In a third preferred embodiment the object to be plated is first shielded with a mask creating or defining a specific free area, e.g. in the form of a spot or stripe. The surface with the mask is subjected to a plating step, after which the mask may be removed and subsequently a second mask is applied covering part of the plated surface, whereafter the object is subjected to the stripping solution.

[0017] The process according to the present invention has several advantages. One advantage is that objects can be obtained with a plating that has a required thickness for there were it is needed and a plating that is thin or even absent on areas where no plating is required.

[0018] In this way plated objects such as loose parts can be obtained that could otherwise not be produced without controlling the plating rate locally. In such conventional processes the plating rate is controlled for example by applying means to the objects to be plated in order to shield the areas on which less plating is desired from the coating process. Applying such means lead to more expensive processes. Moreover, such methods are more cumbersome when the size of the objects to be plated is smaller, and would be very difficult to be carried out with very small objects.

[0019] Another advantage of the process according to the invention is that the metal can easily be reclaimed or recovered from the used stripping solution, for example by simple filtration of a metal salt or by reclaiming the plated metal, e.g. gold, from the cathode. This is especially relevant when the economical value of these metals is high. Preferably, the metal to be plated is a precious metal or an alloy thereof. Suitable and preferred precious metals are gold, silver, ruthenium, palladium, rhodium, platinum and iridium, and mixtures thereof, while the alloys of these metals with cobalt, nickel, iron, indium, thallium, copper, cadmium, and so on, are suitable as well.

[0020] With the process according to the invention it is possible to obtain a plating with a selected distribution in thickness on objects of different shapes and sizes.

[0021] According to the present invention the conditions during the initial plating process are chosen such that the DF value is as low as possible. For objects which are non-uniform, areas of higher current density will generally obtain an initial plating with a higher thickness than the areas of lower current density.

[0022] It is essential in case of complete immersion stripping that during the stripping process the selectivity, for example expressed as the ratio of the rate of removal from the areas where the current density is higher and the rate of removal from the areas where the current density is lower, is higher than the ratio of the two corresponding initial plating rates. In this way, the stripping will result in a final plating on the objects that is thinner on the areas where the current density during stripping was higher than on the areas where the current density during stripping was lower.

[0023] According to the invention this can be obtained by choosing suitable stripping conditions, optionally combined with suitable stripper formulations.

[0024] The initial plating is applied using conventional electrolytic plating processes. Loose part plating can be performed using e.g. vibratory equipment or barrel equipment or any other means to plate loose parts. In all cases these loose parts are being completely exposed to the plating solution. In case of other objects selectivity in plating may be obtained with techniques such as controlled immersion, reel to reel applications for connector reels, or spot galvanising by using masks. The electrolytic plating process is carried out using solutions comprising the ion of the metal to be plated and additional ingredients which influence the initial metal distribution required for the specific applications. After all, metal distribution is not only dependent on geometrical factors buts also on chemical and electrochemical factors and compositions. AUTRONEX HSV, AUTRONEX 2910, are the preferred processes for loose part plating, yielding the lowest initial DF values, although also baths containing other ingredients such as potassium and/or ammonium sulphate and/or sulfamates, chelating agents, metal salts such as cobalt and nickel salts and conducting salts, or other processes such as Autronex™ CC and/or Omega™ C can be used. Additives used in Autronex baths are described in e.g. US-A-5,169,514.

[0025] The stripping process can be conducted in a similar process step, the important difference being the reversal of the current. In the stripping process the plated object is contacted to the anode and submerged in a solution, esp. in an aqueous solution, comprising phosphates, esp. monophosphates, hydroxides, sulfamates, cyanates and/or thiocyanates of alkali metals, e.g. sodium or potassium, or ammonium; or thiourea or derivatives thereof. Stripping can preferably be conducted in a process like Metalex™ EL-M. The basis of Metalex EL-M is a mixture of sodium thiocyanate

and sodium hydroxide. This stripping bath is especially suitable for gold. In addition this stripping bath may contain conventional additives to manipulate the stripping behaviour (e.g. the conductivity, organic adsorbents, etc.) where needed.

[0026] The main requirement of the material of the objects to be plated by the process of the present invention is that they are electrically conductive. Metal objects will therefore be preferred. The size of the objects to be plated is not a limiting factor. Even small objects, especially smaller than 25 mm and even smaller than 5 mm can be plated in the plating process according to the invention.

[0027] The substrate material can be any electrolytically plateable metal. When desired, the stripped material can be recovered from the stripping solution with economical advantage. Recovering of the material will be especially beneficial when noble metals, such as gold, silver, platinum, palladium or rhodium are used.

[0028] The shape of loose parts to be used in the process according to the present invention has to be non-uniform, for example objects that comprise an inner and an outer surface. Preferred shapes are open cylinders, cup-shaped objects and flat objects comprising at least one hole.

[0029] For example, gold plated female connectors are objects that are especially suitable to be manufactured with the process according to the present invention. Due to their small size, such connectors are plated preferably in large amounts simultaneously, for instance several thousands per batch. Since the gold plating is only required on the inside of such connectors, producing these connectors with less gold plating or even no gold plating at all on areas where it is not required can be of great economical advantage. Producing female connectors with a gold plating that is selectively formed on the inside is enabled by the present invention.

[0030] With the process according to the present invention it is possible to manufacture a gold plated connector in which the ratio of metal plating thickness of the outer surface to the metal plating thickness of the inner surface is 0.75 or less.

[0031] Small objects, such as loose parts, can suitably be plated in a barrel, and especially a vibrating barrel, provided with means to contact each of the objects at least for a part of the plating time or stripping time with an electrode. A suitable example is a vibrobot. A vibrobot barrel is basically an open circular basket with a bottom electrode. The loose parts are put in the basket and the total is immersed in the plating or stripping solution. The basket then is vibrated with such frequency and amplitude, that the parts start rotating around the periphery of the basket. The bottom has a shape of half a turn of a screw so when the parts rotate they tumble and mix every time they fall over the edge. The bottom electrode is the cathode when plating and the anode when stripping.

[0032] In the process of the present invention, step (b) is generally carried out at temperatures between 10 and 80°C, although these temperature ranges do not give an essential limitation. Preferably step (b) is carried out at a temperature of between 30 and 60°C.

[0033] When loose parts, or other small objects having a non-uniform surface, are to be stripped, step (b) is generally performed using a current density of 0.01 - 4A/dm^2, preferably of 0.1 - 2A/dm^2.

[0034] The current density is generally in the range of 1 - 100 A/dm^2, and preferably between 2 and 50 A/dm^2 when larger objects have a less complicated shape are to be plated. More in particular, these current densities can suitably be used when the controlled immersion technique or the spot stripping technique in accordance with the second and third preferred embodiment of the present invention, is carried out.

[0035] The duration of the stripping step can vary between 5 seconds and 30 minutes or more, preferably between 30 seconds and 10 minutes. It depends on the applied current density but also on other parameters in the stripping process. In the light of the information given in this specification the person skilled in the art will have the knowledge and tools to find suitable conditions.

[0036] Favorable stripping conditions may be obtained by optimisation of process parameters like current density, stripper temperature, immersion time, (solution) agitation and other factors such as stripper composition. Metalex-EL-M has proved to be effective for this application.

[0037] Large quantities of objects can be produced in a batch-wise or continuous process according to invention. An example of a batch-wise process uses a rotating barrel in which loose parts are placed. The barrel used in the plating process is provided with means to contact the objects with the cathode. This can be obtained for instance by using a basket which comprises holes and by placing the cathode in contact with these loose parts. The anode is in contact with the electrolytic liquid. By rotating the barrel or the basket, the objects will be mixed with the solution and at the same time a fraction of all objects will contact the cathode, thus ensuring a plating on each object with a thickness that is uniform with respect to all objects present in the batch.

[0038] During the stripping, a similar set-up can be applied, in which the object is contacted to the anode and the stripping liquid to the cathode. Homogeneous mixing of the objects is again obtained by rotating the barrel or the basket.

[0039] Instead of rotating the barrel or the basket in the plating and/or the stripping step, it is also possible to use a vibrating barrel which ensures homogeneous processing by suspending each object for about the same fraction of the process time of the entire step.

[0040] In a preferred embodiment, a so-called vibrobot barrel is used. A vibrobot barrel is basically an open circular

basket with a bottom electrode. The loose parts are put in the basket and the total is immersed in the plating or stripping solution. The basket then is vibrated with such frequency and amplitude, that the parts start rotating around the periphery of the basket. The bottom has a shape of half a turn of a screw so when the parts rotate they tumble and mix every time they fall over the edge. The bottom electrode is the cathode when plating and the anode when stripping.

[0041] The current required in the plating process can be advantageously applied as a pulsed current. The duty cycle for pulse plating (on/off) must be optimised for each individual application. Typically, pulses of the type 900 msec on, 100 msec off are used.

[0042] It is also possible to perform the plating process according to the present invention in a continuous process, although continuous processing of loose parts, in a barrel or by vibratory technique, is not likely.

[0043] However, the process of the present invention can be a continuous controlled immersion plating and stripping process or a continuous spot plating an stripping process. In reel to reel connector or lead frame plating a strip of connectors is pulled through a series of process baths. The connector strips are supplied on reels. At the beginning of the process line the strip is unwinded and at the end wound up again. In the process tanks, particularly in the plating and stripping section, techniques like controlled immersion or spot processing may be used. This embodiment is described in figure 1.

[0044] In figure 1a, connector strips are brought in a gold bath. Figure 1b shows immersion of the gold plated strips in a stripping solution, while figure 1c shows the end result: gold plate on the grey area only.

[0045] In the plating solution and stripping organic additives may be present. These organic additions are electrochemically active in (depending on the additive) high or low CD regions and influence the current density gradients and so the thickness distribution. Current density is not only determined by the geometry of the body and the position and shape of the counter electrode, but also by the chemical composition of the plating/stripper solution (primary respectively secondary current distribution). Examples of such additives are given in US-A-5.169.514.

[0046] The invention will be illustrated by the following examples which are included for the purpose of illustration and are not intended to limit the scope of the invention.

Examples

Example 1

[0047] 150 g sockets (total approximate surface area 30 dm^2; the individual sockets having a length of 2.25 mm, the widest diameter (see fig. 2) being 1 mm, the smallest diameter being 0.65 mm, and being made from leaded brass) were gold plated using a bath of deionized water having a conductivity of less than 3 μ-Siemens) to which was added 600 ml/l Autronex™ CC B, 2 g/l PPS (1-(3-sulfopropyl-pyridinium betaine), 16 g/l IQPS (1-(3-sulfopropyl)-isoquinolinium betaine), and 40 g/l $(NH_4)SO_4$. This bath was used with the sockets in a vibrobot set-up having a volume of 5 dm^3 at 35°C for 4 hours at a current density of 0.015 A/dm^2

[0048] A uniform plating thickness of 2 μm was obtained, as measured using X-ray fluorescence spectroscopy (XRF). The distribution, factor (DF) which is defined here as the average thickness of the plating on the outside of the object divided by the average thickness of the plating on the inside of the object was 1.

[0049] Two stripping solutions of the following compositions were made:

Solution 1: 7.5 g/l sodium hydroxide and 70 g/l sodium thiocyanate in demineralized water (having a conductivity of less than 4 μ-Siemens).

Solution 2: 50 g/l potassium mono phosphate, 40 g/l sodium hydroxide and 55 g/l sodium thiocyanate in demineralized water (having a conductivity of less than 4 μ-Siemens).

[0050] The sockets were subjected to three different stripping procedures:

Procedure 1: Solution 1; 150 g sockets (total surface area 30 dm^2), 0.4 A/dm^2, 40°C, 12 minutes; DF before stripping 1.0, DF after stripping 0.8); after the stripping process a gold flash was used (AUROBOND TN); this gold flash covering the areas, which were gold stripped completely, with a yellow color (≤ 0.05 μm Au); the function of this gold flash being the provision of corrosion resistance and a cosmetic effect;

Procedure 2: Solution 2; 100 g sockets (total surface area 20 dm^2), 0.3 A/dm^2, 6 minutes, room temperature; DF before stripping 0.95, after stripping 0.85;

Procedure 3: Solution 2, (total surface area 20 dm^2), 0.3 A/dm^2, 18 minutes, room temperature; DF before stripping 1.0, after stripping 0.85).

[0051] The DF-values are measured by determining the thickness of the plating on 16 randomly chosen places at 16 randomly picked different sockets by using XRF. The results are summarized in Figures 3 - 5.

Example 2

[0052] 150 g sockets (surface area 30 dm^2) were gold plated using a gold bath (Autronex™ CC (cobalt hardened gold)) having a gold concentration of 1 g/l, in vibratory equipment (see example 1) at a temperature of 35°C and a current density of 0.1 A/dm^2, for 60 minutes. The plated sockets obtained had an average thickness of 1.15 µm and a DF of 1.

[0053] Subsequently, the sockets were subjected to a stripping step using Metalex stripper bath Metalex™ EL-M containing 5 - 40 g/l sodium hydroxide and 55 g/l sodium thiocyanate under the following conditions:

Procedure 1: 75 g sockets having a surface area of 15 dm^2; 0.3 A/dm^2, 6 minutes at 40°C;
Procedure 2:75 g sockets having a surface area of 15 dm^2, 1.6 A/dm^2, 3 minutes at 40°C.

[0054] The following results were obtained:

Table 1

Plating thickness of Example 2.				
	Procedure 1		Procedure 2	
Measurement No.	Thickness Inside µm	Thickness Outside µm	Thickness Inside µm	Thickness Outside µm
1	0.69	0.56	0.84	0.08
2	0.66	0.39	0.88	0.36
3	0.65	0.49	0.87	0.27
4	0.61	0.37	0.94	0.39
5	0.69	0.54	0.88	0.27
6	0.72	0.44	0.98	0.37
7	0.99	0.44	0.71	0.23
8	0.50	0.49	0.86	0.15
9	0.64	0.31	0.81	0.36
10	0.50	0.52		0.40
11	0.74	0.53		0.26
12	0.58	0.56		0.32
13		0.56		
14		0.52		
15		0.41		
16		0.46		
Mean	0.696	0.475	0.863	0.288
DF	0.68		0.33	

Example 3

[0055] While using the equipment of example 1, 150 g sockets (surface area 30 dm^2) were gold plated by using an Autronex™ HSV (2 g/l Au) plating bath, pH 4.8, room temperature, 0.05 A/dm^2, 35 minutes. subsequently, the plated sockets were subjected to a stripping step using different versions of METALEX EL-M (as identified in table 2).

Table 2

Plating thickness of Example 3								
No.	EL-M	Temp	I	t_{strip}	[Thio-urea]	Plating Thickness		DF
	[wt.%]	[°C]	[A]	[min]	[g/dm^3]	Inside [μm]	Outside [μm]	[-]
1	50	35	2.6	7	0	0.57	0.37	0.66
2	50	30	1.3	10	0	0.57	0.47	0.82
3	50	50	1.3	10	0	0.67	0.67	1
4	50	50	1.3	10	2	0.98	0.98	1
5	50	50	2.6	10	2	0.98	0.98	1
6	50	50	5.0	10	2	0.65	0.61	0.93
7	50	25	2.6	25	0.2	0.252	0.325	0.6
8	65	25	2.6	10	0.2	0.54	0.58	1.05
9	65	25	1.3	20	0.2	0.48	0.46	0.97
10	25	25	2.6	15	0	0.5	0.48	0.97

Claims

1. Process for plating an object, having wanted and unwanted areas to be plated, comprising the steps of

   a) forming in a plating bath of a plating on the surface or a selected part of the surface of said object, yielding a certain DF value;
   b) partially restripping of the plating of step a) in an electrolytic stripping process using a stripping solution under such conditions that said DF value is lowered.

2. The process of claim 1, wherein the total surface is plated, and wherein the total surface is partially restripped and wherein the DF value is lowered through a difference in current distribution during stripping.

3. The process of claim 1, wherein the object is fully or partly immersed in a plating bath, and subsequently partly immersed in a stripping solution.

4. The process of claim 1, wherein the object is shielded with a mask defining a specific free area, and additionally subjected to the plating step and subsequently applying a second mask before the object is subjected to the stripping solution.

5. Process according to any of the preceding claims wherein the stripped material formed in step b) is recovered.

6. Process according to any of the preceding claims wherein the metal plating is formed from a metal selected from the precious metals or alloys thereof.

7. Process according to any of the preceding claims wherein said objects have an inner and an outer surface and are preferably selected from the group consisting of hollow cylinders, sockets and cup-shaped objects.

8. Process according to any of the preceding claims wherein step b) is performed in the presence of an aqueous solution comprising monophosphate, hydroxide, thiocyanate, cyanate anions and/or thiourea or derivatives thereof, or in a Metalex EL-M stripping bath.

9. Process according to any of the preceding claims wherein step b) is performed at a temperature of 10 - 80°C, preferably of 30 - 60°C.

10. Process according to claim 2 wherein step b) is performed using a current density of 0.01 - 4 A/dm^2 in a barrel or vibrating container.

11. Process according to claim 2 or claim 3, wherein step b) is performed having a current density of 1 - 100 A/dm^2.

12. Process according to any of the preceding claims wherein step b) is performed for a period of between 5 seconds to 30 minutes, preferably of between 30 seconds and 10 minutes.

13. Object obtainable by the process of any one of claims 1 - 12 having a DF value of 0.75 or less.

14. Use of a stripping solution in a plating process to lower the DF value.

Fig. 1a

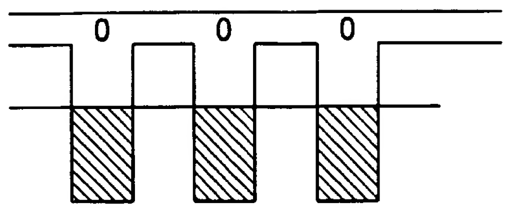


Fig. 1b

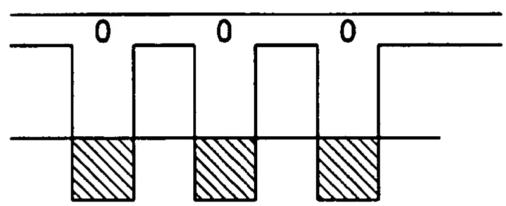


Fig. 1c

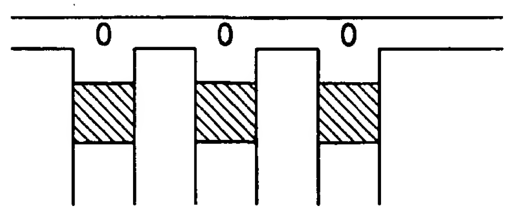
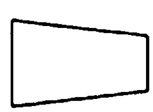


Fig. 2



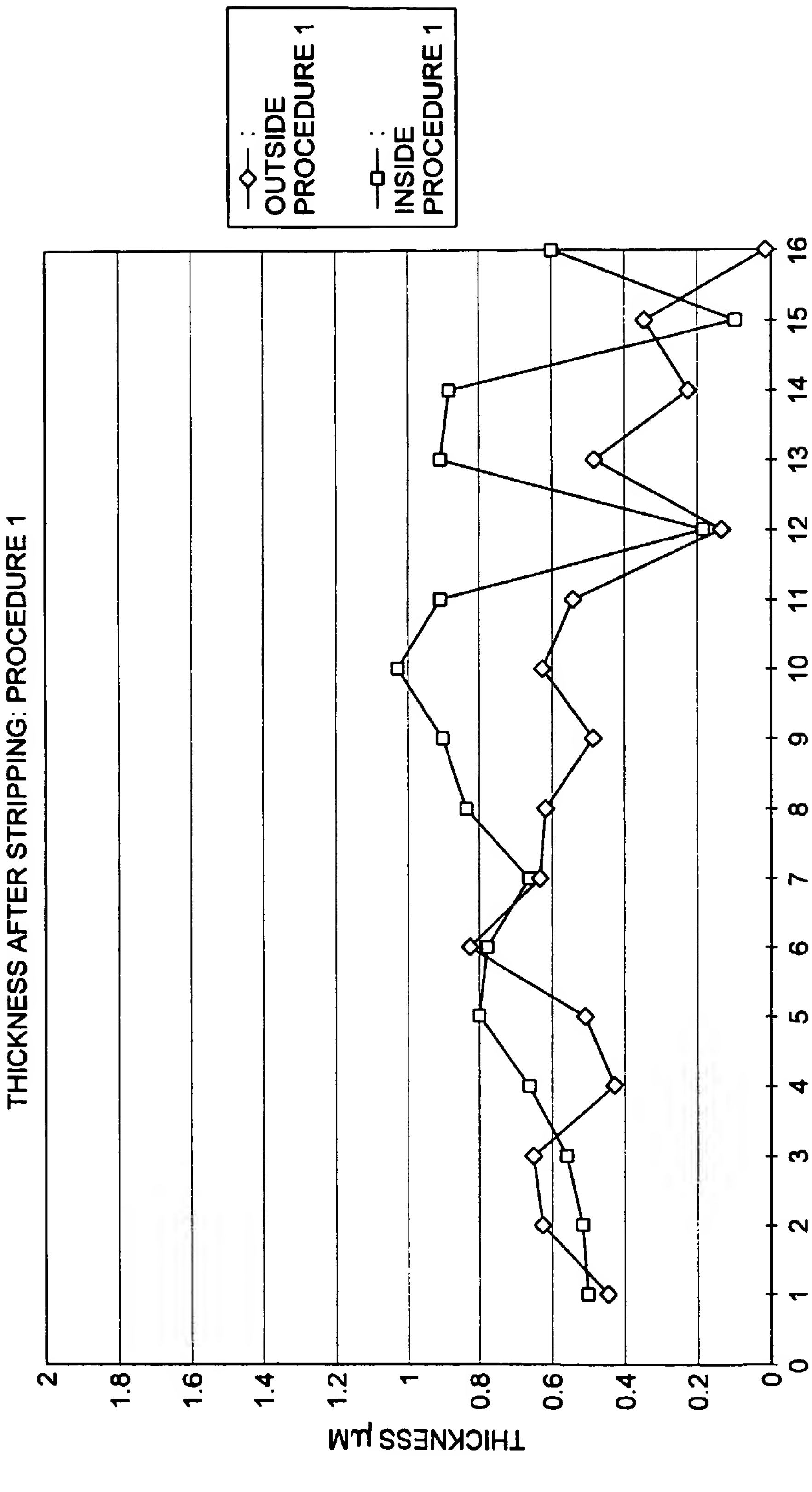

THICKNESS AFTER STRIPPING: PROCEDURE 1
THICKNESS µM
MEASURING POINT
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
OUTSIDE PROCEDURE 1
INSIDE PROCEDURE 1

Fig. 3

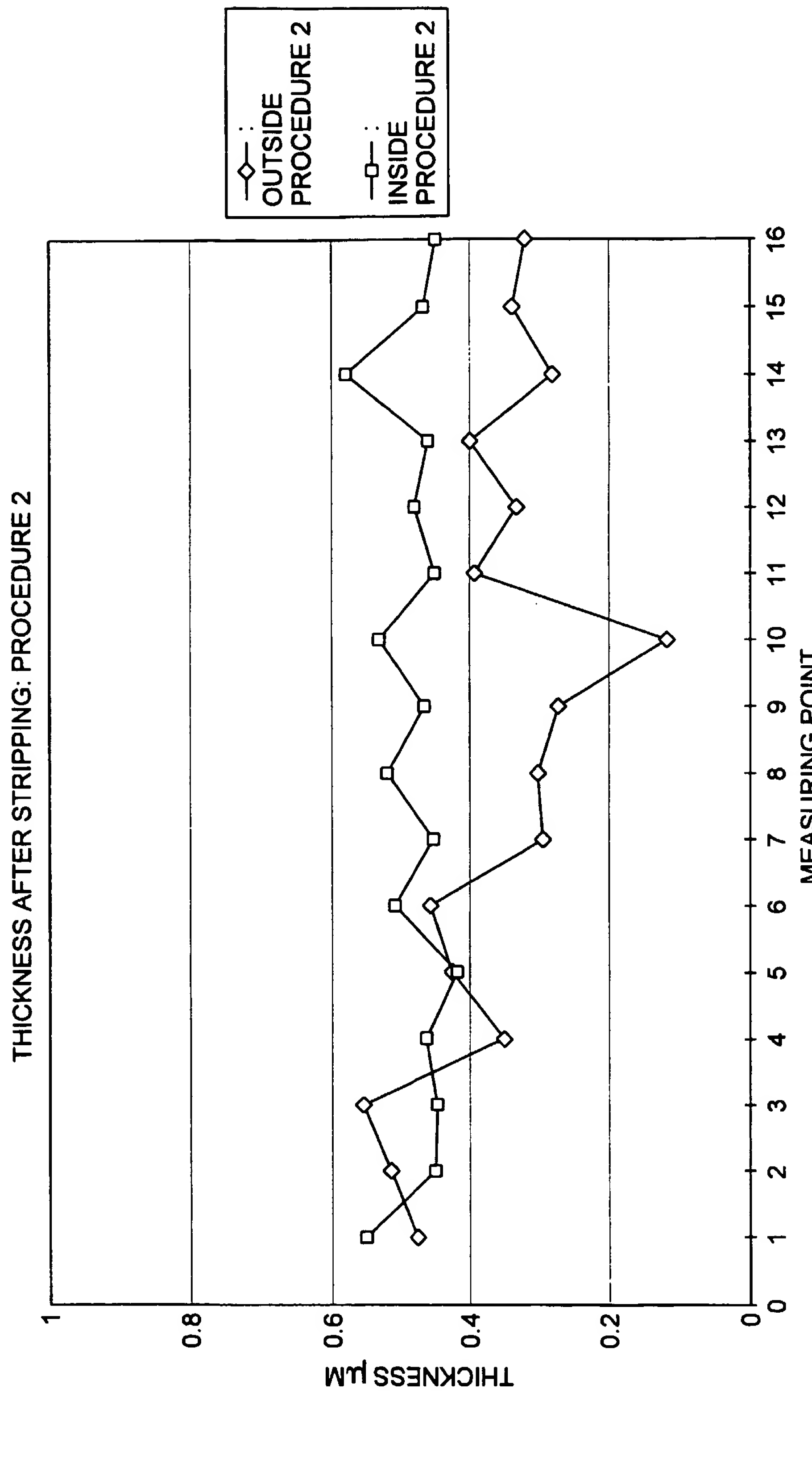

THICKNESS AFTER STRIPPING: PROCEDURE 2
OUTSIDE PROCEDURE 2
INSIDE PROCEDURE 2
THICKNESS µM
MEASURING POINT
0
0.2
0.4
0.6
0.8
1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

Fig. 4

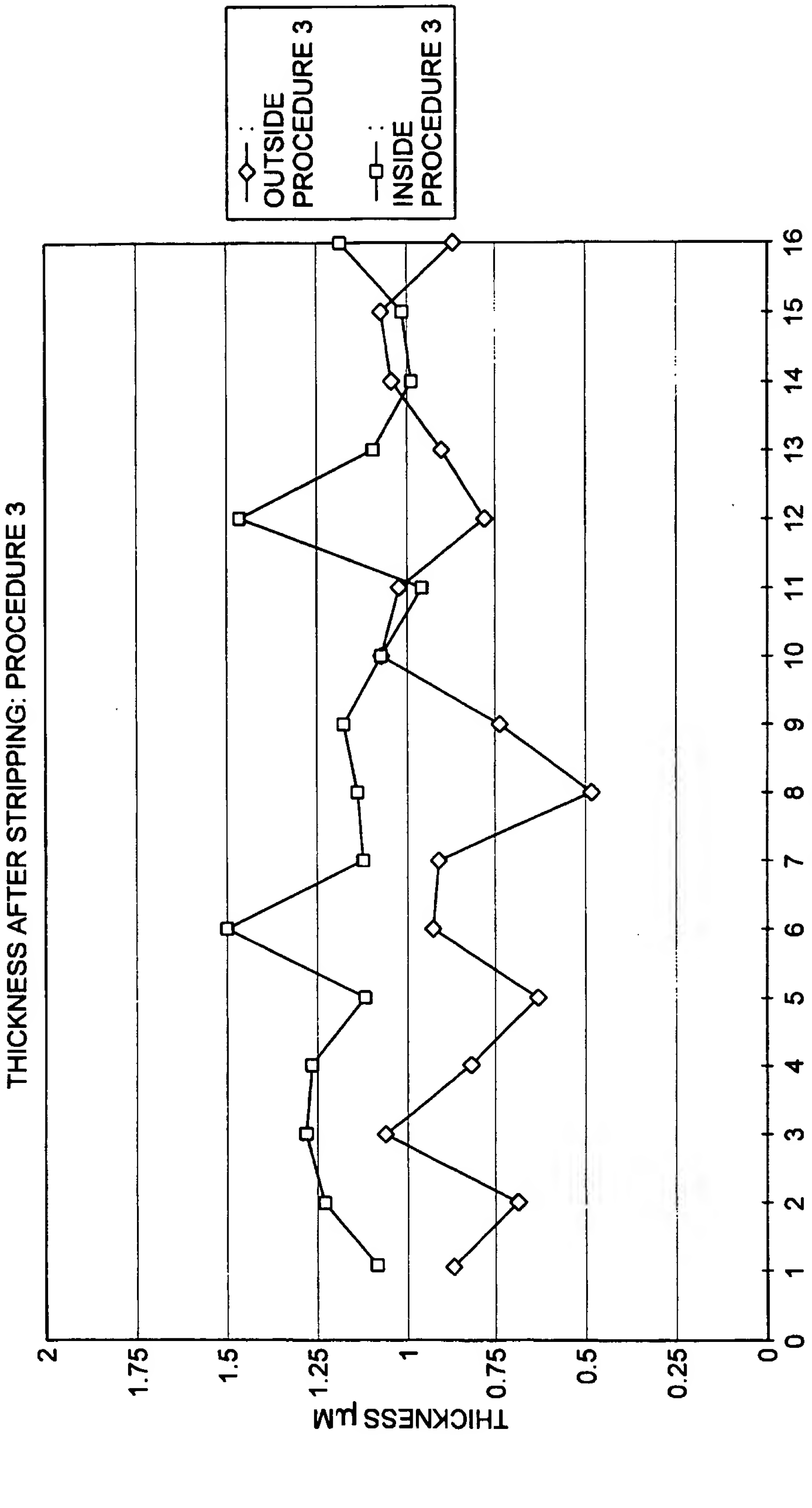

THICKNESS AFTER STRIPPING: PROCEDURE 3
THICKNESS µM
MEASURING POINT
OUTSIDE PROCEDURE 3
INSIDE PROCEDURE 3
0
0.25
0.5
0.75
1
1.25
1.5
1.75
2
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

Fig. 5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 2857

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 410 955 A (ANDRITZ AG MASCHF) 30 January 1991 (1991-01-30) * claims 1-4 *	1,2,5	C25D7/00 C25D5/02 C25F5/00
X	US 5 098 534 A (NAKAMURA TAICHI ET AL) 24 March 1992 (1992-03-24) * column 1, line 5 - column 2, line 2 * * column 3, line 19-25 *	1-4,6,7	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
C25D
C25F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 February 2000	Van Leeuwen, R

CATEGORY OF CITED DOCUMENTS

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